Anal. Calcd for $C_{27}H_{32}O_{12}$: M_r 548.1894. Found: M_r (MS) 548.1915.

Aldehydes 1b and 2c. A sample of 3 mg of each of **1a** and **2a** was dissolved in 3 mL of ether and shaken at room temperature for 1 h with about 100 mg of activated MnO_2. After filtration and evaporation, the NMR spectra of the residual gums, **1b** and **2c**, were obtained at 270 MHz without further purification (Table I). The spectra indicated complete conversion of **1a** and **2a** into **1b** and **2c**, respectively.

Melcanthin C (3a). A second collection of *M. leucanthum*, Stuessy No. 3829, made in Grant County, N. Mex., 1.4 mile west of Silver City on Highway 260 on September 9, 1975, provided, by the above extraction procedure, 13 g of crude syrup which was chromatographed over 300 g of silica gel using *n*-propyl acetate as eluent, with 20-mL fractions being collected. Rechromatography of fractions 71–79 over 20 g of silica gel using $CHCl_3$–*n*-propyl acetate (3:2) as eluent yielded in fractions 63–75 90 mg of melcanthin C as a gum: CD (*c* 2.43×10^{-4}, MeOH) $[\theta]_{214}$ -1.64×10^4, $[\theta]_{239}$ $+1.13 \times 10^3$, $[\theta]_{261}$ -5.75×10^2; IR ν_{max} ($CHCl_3$) 3500, 1760, 1740, 1720, 1230, 1130 cm^{-1}. The low-resolution mass spectrum (70 eV) showed significant peaks at *m/e* (relative intensity) 452 (0.2, M^+), 392 (0.3, M − 60), 364 (0.7, M − 88), 304 (4.0, M − 60 −88), 71 (62.0), and 43 (100.0).

Anal. Calcd for $C_{22}H_{28}O_{10}$: M_r 452.168. Found: M_r (MS) 452.167.

Acknowledgments. Work at Louisiana State University (N.H.F.) was supported by Grant No. 1-R01-CA 19800, awarded by the National Cancer Institute, DHEW, and, in part, by a grant from the National Science Foundation to N.H.F. (DEB-76-20585). One of us (N.H.F.) wishes to express his gratitude to Professor F. Bohlmann, Technical University, Berlin, Germany, for his hospitality during the Fall Semester 1977. A number of spectral data obtained in his institute enabled the authors to complete this paper. The authors also wish to thank Dr. Zeisberg (Berlin) for low-temperature NMR spectra and Drs. D. L. Perry and D. M. Desiderio for obtaining some mass spectral data at the Institute of Lipid Research, Baylor College of Medicine, Houston, Texas.

Registry No.—**1a**, 68024-34-0; **1b**, 68024-35-1; **2a**, 68024-36-2; **2b**, 68024-37-3; **2c**, 68024-38-4; **3a**, 68024-39-5.

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(5) N. H. Fischer, R. A. Wiley, D. L. Perry, and K. D. Haegele, *J. Org. Chem.*, **41**, 3956 (1976).
(6) In our previous publication,[4] a 4,5-trans double bond was assigned to melampodin B mainly on grounds of its cooccurrence with melampolides of known absolute configuration containing a 4,5-trans double bond. Furthermore, large coupling constants ($J_{5,6}$ = $J_{6,7}$ = 10 Hz) in the NMR spectrum of melampodin B indicated an antiperiplanar orientation of the three protons. However, the NMR absorption of the C-15 aldehyde proton (9.49 ppm) of the melampodin B derivative suggested a 4,5-cis double bond.[8] X-ray data obtained by Professor S. F. Watkins and collaborators provided unambiguous evidence that melampodin B contains a 4,5-cis double bond and a C-1α acetoxy moiety. The correct structure for melampodin B is represented by **4**.
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(13) N. H. Fischer, R. Wiley, and J. D. Wander, *J. Chem. Soc., Chem. Commun.*, 137 (1972).
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Mechanism of the Rearrangement of 5,6-Disubstituted-dibenzo[*a*,*e*]cyclooctatetraenes to the 5,11-Isomers[1]

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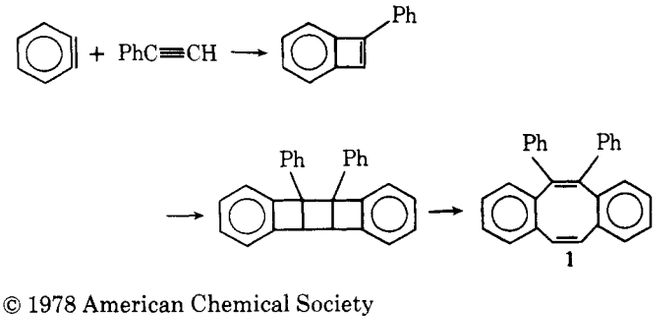
Received May 2, 1978

The previously reported rearrangement of 5,6-disubstituted-dibenzo[*a*,*e*]cyclooctatetraenes to the 5,11-isomers has been shown to proceed via biradical intermediates. The biradicals derived from the 5,6-diphenyl and 5,11-diphenyl representatives were trapped by reaction with benzenethiol, and the structures of the resulting reduction products were established by chemical and spectroscopic data and by comparison with known compounds. The rate of reaction of **1** with butanethiol was similar to its rate of rearrangement, indicating that the two processes required a common intermediate, the biradical **4**.

Benzyne, generated under the appropriate conditions, undergoes reaction with acetylene derivatives to give dibenzocyclooctatetraenes.[2] The reaction is illustrated by the formation of 5,6-diphenyldibenzo[*a*,*e*]cyclooctatetraene (**1**), a compound of central interest to the present paper.

Investigation of the thermal behavior of **1** and related compounds such as the 5,6-dicarbomethoxy analogue led to the discovery of a novel rearrangement.[3] When heated, the starting materials are smoothly rearranged to the 5,11-isomers; e.g., **1** yields **2**.



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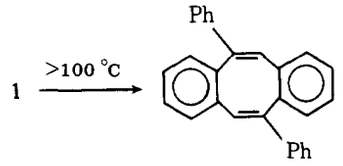
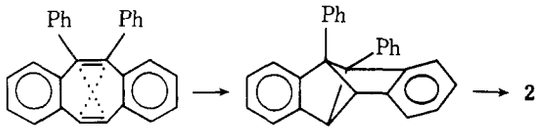


2

The rearrangement proceeds in high yield, is irreversible, and can be photolytically effected as well. Photolytic yields are considerably lower than thermal ones, with other products attending the formation of the 5,11-isomer. Although the work described here concerns the thermal rearrangement mechanism, certain parallels were found in a subsequent study of the photochemical mechanism.[4]

Crossover experiments[3] ruled out the possibility that the rearrangement occurs by a dissociation–recombination pathway such as reversal to benzocyclobutadiene, head-to-tail dimerization, and ring opening. These results pointed to an intramolecular pathway, and one such mechanism, postulated in the initial report of the rearrangement, invoked a tricyclic intermediate. For the isomerization of 1 to 2 the intermediate would be 3.



1 3

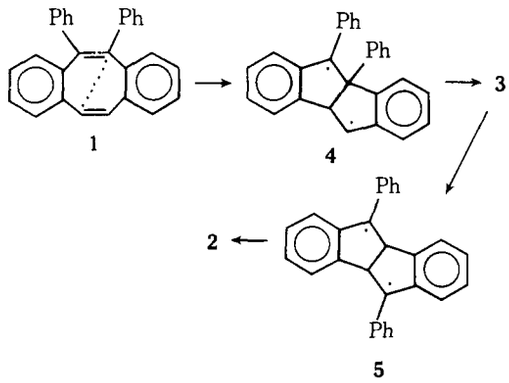
A search for the intermediate 3 was made[3] by analysis of reaction mixtures derived by heating 1 for limited periods of time; however, only 1 and its rearrangement product (2) were found. These results were presumed not to rule out 3 since it should possess substantial strain energy. The parent tricyclooctadiene has been found to be highly labile at room temperature.[5,6]

The working postulate of the present investigation was based on the possibility that the rearrangement proceeds by way of biradical intermediates. As applied to the isomerization of 1 to 2, the postulated mechanism may be summarized as in Scheme I.

Results and Discussion

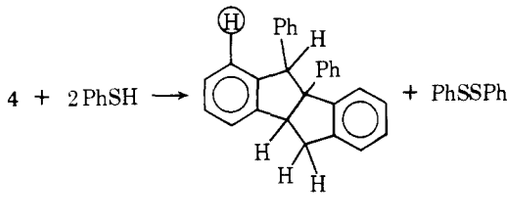
A. Trapping of the Biradical Intermediates with Benzenethiol. The avidity with which many organic radicals abstract hydrogen from a sulfhydryl group is well established, and the reaction has been widely exploited in the trapping of free radicals.[7] The ability of thiols to intercept radicals is a result in part of the very low activation energy, less than 10 kcal/mol, for the hydrogen abstraction process.[8] In our case, the interception of the biradical 4 would only succeed if its rate of reaction with thiol was considerably greater than rates of subsequent rearrangement steps.

Scheme I



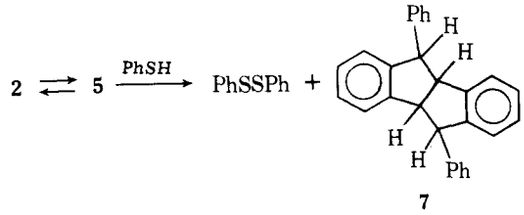
When a dilute solution of 1 in benzenethiol was refluxed for a period of time representing several rearrangement half-lives, workup of the reaction mixture provided phenyl disulfide (85%), small amounts of yellow oils which were not investigated,[9] and a colorless hydrocarbon (63%). The hydrocarbon crystallized to well-formed prisms, but repeated chromatography and recrystallization gave material melting at 129–136 °C. The hydrocarbon most likely is a mixture of stereoisomers.

The molecular formula of the hydrocarbon, $C_{28}H_{22}$, represented the addition of 2 hydrogen atoms to the cyclooctatetraene reactant. The UV spectrum showed only weak absorption bands characteristic of unconjugated benzenoid chromophores, and the IR spectrum had prominent bands characteristic of mono- and ortho-substituted benzene. If the biradical 4 was intercepted by thiol, the expected structure of the hydrocarbon is 6. Excluding enantiomeric pairs, and if the central ring fusion is cis, a reasonable assumption on mechanistic grounds, the number of possible isomers is two, in which the two phenyl groups are either cis or trans.



The data given are consistent with the anticipated structure 6, and additional evidence is found in the ^1H NMR spectrum, although its interpretation was not straightforward. An ABX pattern, assigned to the methylene and neighboring methine hydrogens, was readily discernible as was a singlet, assigned to the isolated methine hydrogen. The unusual feature of the spectrum consisted of an unsymmetrical doublet of doublets (J_1 = 8 Hz, J_2 = 1 Hz) centered at δ 5.8 which integrated for one proton. The fact that the aromatic region integrated for only 17 protons and the gross appearance of the signal and its associated coupling constants implicated one of the aromatic protons; however, the high-field position of the signal demanded an unusually strong shielding environment. Stereochemical models suggest that the most likely candidate is the proton circled in the structural formula; the models reveal that it resides in the shielding region of the proximal phenyl group. The identical signal, but with twice the intensity, reappeared in spectra of products trapped from the reaction of the 5,11-isomer, and the NMR spectrum of a forthcoming model compound supported the assignment (vide infra).

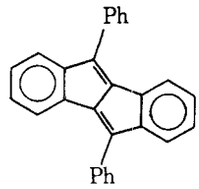
The results of the trapping experiments with the 5,6-isomer suggested an examination of the behavior of the 5,11-isomer toward thiol. Although the overall rearrangement is irreversible, it was argued that the final step might not be. In such an event the isomeric biradical (5) might be trapped by thiol to give a new reduction product (7).



When the trapping experiment was repeated with the 5,11-isomer, the reaction mixture furnished phenyl disulfide (84%), a small amount of yellow oil[10] which was not investigated, and a solid hydrocarbon. This hydrocarbon also had the molecular formula $C_{28}H_{22}$, and its UV and IR spectra were

similar to those of the 5,6-trapping product, but a comparison of the upfield portions of the NMR spectra left no question that a new product had been obtained,[11] although, again, the unusual signal at δ 5.8 was present; its intensity now accounted for two protons.

Structural assignment of the new reduction product was greatly facilitated by the fact that three of the stereoisomers of **7** had been prepared previously by Brand[12] by sodium/alcohol reduction of the well-known diphenyldibenzopentalene **8**.

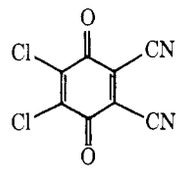


+ Na/EtOH ⟶ **7**

8

Brand's synthesis of **7** was repeated, and the NMR, IR, and UV spectra of the product (not separated into its stereoisomers) were identical with those of the trapping product of the 5,11-isomer. The identity of Brand's reduction product with our 5,11-trapping product was confirmed by a dehydrogenation experiment. When the 5,11-trapping product was treated with 1,2-dichloro-5,6-dicyanoquinone (DDQ), the expected pentalene derivative **8** was obtained in good yield.

5,11-trapping product (**7**) +



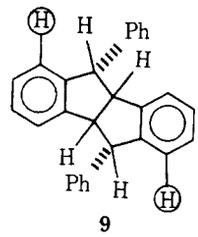
DDQ

⟶ **8** + DDQ · H_2

These results established unambiguously the structural assignment of the trapping product of the 5,11-isomer and lend considerable weight to the conclusions regarding the structure of the 5,6-trapping product.

In order to place the interpretation of the NMR spectra on a more secure footing, the all-cis stereoisomer **9** was prepared by catalytic hydrogenation of **8**.[13]

8 + 2H_2 —Pd/C→

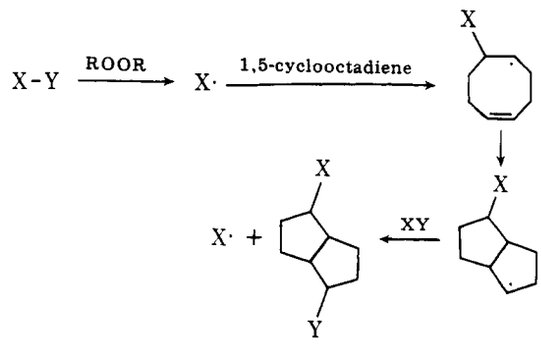


9

The NMR spectrum of this isomer exhibited the expected symmetrical A_2B_2 array for the 4 methine protons, a complex multiplet at δ 6.55–7.42 accounting for 16 of the aromatic protons, and the doublet of doublets signal centered at δ 5.8 integrating for 2 protons, which we assigned to those circled protons in the structural formula of **9**.

The chemical genesis of the trapping products, composition data, spectral comparison with model compounds, and dehydrogenation results leave little question about the authenticity of the proposed structures.

B. Kinetics of the Trapping Reactions. An important objection to the interpretation of the trapping experiments may be raised, and that is the possibility that thiol reacts with the cyclooctatetraene substrates by a pathway independent of the rearrangement. Dowbenko[14] and Friedman,[15] for example, have shown that addition of certain compounds to 1,5-cyclooctadiene can be initiated by peroxides and that this reaction proceeds by way of a chain-radical mechanism.



Since this reaction obviously bears some resemblance to our trapping reactions, it became necessary to test the possibility that such a mechanism, or some other nonrearrangement process, might be responsible for the trapping results. A kinetic analysis provided such a test.

The rates of the trapping reactions were measured by heating the cyclooctatetraene substrate in neat butanethiol. Concentrations of substrate were conveniently monitored by UV spectroscopy. The cyclooctatetraenes absorb strongly compared to the trapping products, so that rates could be measured by following the diminution of absorbance.

The reactions of both the 5,6- and 5,11-isomers with butanethiol were found to be first order with respect to the cyclooctatetraene concentration. The rate constants of the reactions along with that of the rearrangement are shown in Table I.

It can be seen that the rate of trapping with the 5,6-isomer is comparable in magnitude to its rate of rearrangement, suggesting, at minimum, that the two reactions are not kinetically inconsistent. It is very likely that both reactions involve a common rate-determining intermediate, presumably the biradical **4**. It is therefore unlikely that the reaction with thiol occurs by a pathway independent of the rearrangement, as, for example, a chain radical mechanism. Such a possibility would only be tenable if the rate of trapping was very much faster than rearrangement.

The fact that the rearrangement rate is approximately twice as great as the corresponding trapping rate requires comment. If the biradical mechanism is correct, the rearrangement cannot, of course, proceed faster than the formation of the initial biradical. We explain this discrepancy by noting that the trapping reaction of the 5,6-isomer, as well as the 5,11-isomer, is not as clean as the rearrangement. Since yellow oils were found along with the expected reduction products, absorption of ultraviolet light would lead to an apparent diminution of the trapping rate. Furthermore, the rearrangement rate is an extrapolated value. This fact alone may very well account for the difference in rates.

The results of the trapping experiments point rather convincingly to the validity of the biradical rearrangement mechanism. Given the well-established precedents of thiol–radical reactions, the structures of the trapping products, and the associated rate comparisons, mechanistic alternatives seem unlikely. Furthermore, some earlier reports on the

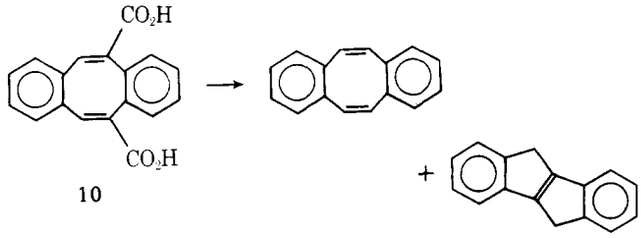
Table I. Rates of Rearrangement and Trapping at 174.5 °C

compd	reaction	rate × 10^5, s^{-1}
5,6-isomer (**1**)	rearrangement	11.3[a]
	trapping by butanethiol	6.63
5,11-isomer (**2**)	trapping by butanethiol	4.56

[a] Extrapolated value for data of Stiles and Burckhardt.[3]

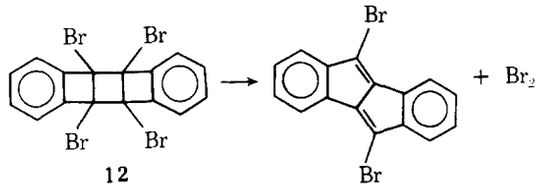
chemistry of dibenzocyclooctatetraenes may be cited to support the present interpretation.

Fieser,[16] in the first synthesis of dibenzo[a,e]cyclooctatetraene, reported the formation of the isomer **11** during the decarboxylation of **10**. The product **11** must obviously arise from transannular interactions in the central ring.



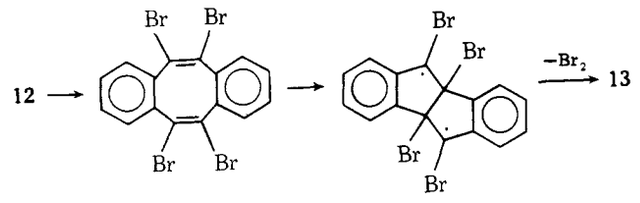
10 **11**

In a somewhat more closely related case, Cava has reported the formation of the dibromopentalene **13** from **12**.[17] Cava



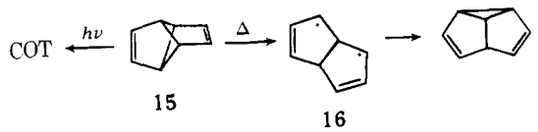
12 **13**

proposed the intervention of the biradical **14** to account for the transformation. This interpretation is clearly consistent with the biradical rearrangement mechanism.



14

Of particular theoretical interest are the reports of Meinwald[5,18] and Zimmerman[6] on the behavior of the tricyclooctadiene **15**. This compound, which is unstable even at room temperature, does not rearrange thermally to COT, but gives semibullvalene instead, apparently via the doubly allylic biradical **16**, which contains the π-electron system central to our phenylated biradical **4**.



15 **16**

Zimmerman[6] has pointed out that the concerted thermal rearrangement of **15** to COT is in fact forbidden by orbital symmetry requirements. Photochemical rearrangement to COT is allowed and has been observed by Meinwald.[18] Rearrangement of the biradical **4** to a semibullvalene may be prevented because it requires loss of aromaticity in one ring, as suggested by Zimmerman.[6] An alternative explanation of the divergent behavior between **16** and its phenylated counterpart **4** rests on the intriguing possibility that the two have different spin states. Meinwald has put forth a similar conjecture to account for the difference between the thermal and photochemical reactions of **15**.[18]

One final note about the rearrangement mechanism should be added, and that is its relationship to the mode of racemization of certain optically active cyclooctatetraenes. We present evidence bearing on this point in the accompanying paper.[21]

Experimental Section

General. Melting points are corrected unless otherwise stated. Microanalyses were performed by Spang Microanalytical Laboratory, Ann Arbor, Mich. A Perkin-Elmer Infracord Model 137 was used to record IR spectra, and UV spectra were determined by use of a Cary Model 11 recording spectrophotometer. Proton magnetic resonance spectra were recorded with a Varian Associates A-60 instrument.

Benzenediazonium 2-Carboxylate. This compound was first prepared by Hantsch and Davidson.[19] Its thermal decomposition to benzyne was discovered by Stiles and Miller.[20] The following procedure, which eliminated the preparation of the intermediate diazonium chloride used by Hantsch, was worked out by Dr. John J. Uebel.

Reaction conditions, reagents, and solvents were kept below 10 °C, and all operations were performed behind a sturdy shield. Amyl nitrite (5 mL) was added in one portion to a solution of anthranilic acid (2.74 g, 0.0200 mol) in absolute alcohol (25 mL), and the mixture was stirred for 2 h. The resulting red solution was poured into a solution of dry ether (50 mL) in absolute alcohol (50 mL). The product was precipitated by adding dry ether (170 mL) and maintaining at ice temperature for 25 min. When collected on a Büchner funnel, the appearance of the product (2.0 g) was that of a tan, finely granular solid or nearly white small needles. The product was used immediately to minimize the danger of explosion.

Samples of the salt which are thoroughly dried and/or stored are especially prone to detonation, but freshly prepared damp samples show no tendency to explode when transferring or when handling in the ordinary way. We emphasize, however, that during its preparation and subsequent use appropriate safety precautions are mandatory.

Formation of 6 from Reaction of 1 with Benzenethiol. A solution of **1**[2] (0.785 g, 0.0220 mol) in freshly distilled benzenethiol (50 mL) was refluxed under nitrogen for 15 h. The excess thiol was distilled at 50 torr under nitrogen. The residue was applied to a column of Florisil (20 × 480 mm) in ligroine (30–60 °C) and eluted with three 100-mL portions of ligroine to give phenyl disulfide (0.410 g, 85.4%). Continued elution of the column with 650 mL of 2% benzene in ligroine gave **6** (0.496 g, 62.7%) as a white solid. Recrystallization of this material from ligroine gave well-formed prisms, mp 129–135 °C. Further attempts to purify this product by successive recrystallization from a variety of solvents and by chromatography on different supports were unsuccessful. The product is presumed to be a mixture of stereoisomers (vide supra): UV (EtOH) λ_{max} 262, 267, 273 nm (ϵ 1800, 2470, 2580); ^{1}H NMR ($CDCl_3$) δ 3.26 (m, 2, CH_2 part of an ABX assembly), 4.18 (m, 1, CH part of an ABX assembly), 5.42 (brd s, 1, lone methine H), 5.8 [dd, 1, J_{ortho} = 8 Hz, J_{meta} = 1 Hz, shielded benzo group H (vide supra)], 6.6–7.6 (m, 17, remaining aromatic protons); IR (KBr) 3040, 2915, 792, 783, 703 cm^{-1}.

Anal. Calcd for $C_{28}H_{22}$: C, 93.81; H, 6.19. Found: C, 93.71; H, 6.26.

Formation of 7 from Reaction of 2 with Benzenethiol. A solution of **2**[3] (0.738 g, 0.00207 mol) in freshly distilled benzenethiol (7 mL) was refluxed under nitrogen for 15 h. Unreacted thiol was removed by distillation with a water aspirator and the residue applied to a column of Florisil (25 × 70 mm) contained in ligroine. Elution with 900 mL of ligroine provided phenyl disulfide (0.381 g, 84%). Successive elution with 50 mL of 4% benzene in ligroine (blank), 500 mL of 10% benzene in ligroine, and 250 mL of 15% benzene in ligroine provided a pale-yellow solid which was rechromatographed on a column of neutral alumina (25 × 300 mm). Elution with 500 mL of 10% benzene in ligroine gave **7** as a colorless crystalline solid (0.549 g, 74%) followed by a fraction of yellow oil (0.151 g), the latter of which was discarded. No attempt was made to separate **7** into its stereoisomers. IR, UV, and NMR spectra were identical with those of the sodium/alcohol reduction product of 5,10-diphenylindeno[2,1-*a*]indene.[12]

Dehydrogenation of 7 with DDQ. A sample of **7** (88.9 mg, 0.248 mmol) was combined with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (223.7 mg, 0.983 mmol) and chlorobenzene (5 mL), and the mixture was refluxed for 10 min. A precipitate of the hydroquinone (84 mg, 74%) was filtered off. The filtrate was treated with 10 drops of benzenethiol to destroy any unreacted quinone, extracted twice with 5% KOH, and dried ($MgSO_4$). Chlorobenzene was distilled at 12 torr, and the solid residue recrystallized from benzene/ethyl acetate to give 5,10-diphenylindeno[2,1-*a*]indene, identified by comparison of its spectra with those of authentic material and by its mixture melting point.

Rates of Reaction of 1 and 2 with 1-Butanethiol. A stock solution of 0.1% of the dibenzocyclooctatetraene in freshly distilled 1-butanethiol was prepared. Aliquots (1 mL) of the stock solution were placed in small test tubes, purged with nitrogen for 2 min, and sealed. The tubes were placed in a thermostated oil bath (174.5 ± 0.5 °C). A tube was removed at approximately 1-h intervals, cooled quickly to

room temperature, and opened. Unreacted thiol was evaporated in a stream of nitrogen and the residue diluted to 50 mL with 95% alcohol. The UV spectrum of the solution was recorded, and the absorbance at 260 nm was used to monitor the reaction rate. First-order kinetics were observed, and rate constants were obtained from the equation $1 + \log (A - A_\infty) = kt$, where A = absorbance at 260 nm and A_∞ is the absorbance at the infinity titer; the latter was obtained from a sample heated for 4 hours at 200 °C (10 half-lives). A least-squares analysis of the data gave rate constant precisions of approximately 7%.

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Registry No.—**1**, 33416-97-6; **2**, 67761-47-1; **6**, 67784-51-4; **7**, 67761-48-2; benzenediazonium 2-carboxylate, 1608-42-0; phenyl disulfide, 882-33-7; amyl nitrite, 463-04-7; anthranilic acid, 118-92-3; benzenethiol, 108-98-5; 1-butanethiol, 109-79-5.

References and Notes

(1) This work is taken from the Ph.D. Thesis of the author, University of Michigan, 1966, a preliminary report of which was presented by M. Stiles, Abstracts, 19th National Organic Chemistry Symposium, Tempe, Ariz., June 13–17, 1965, pp. 57–62.
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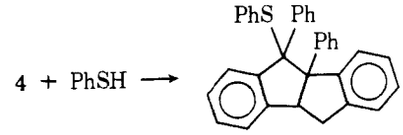
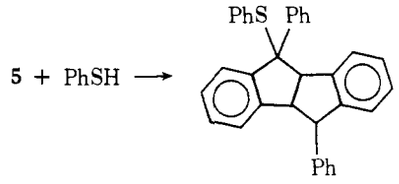
(9) Although these oils were not characterized, material balance data suggest that they, and those found in the reaction of **2** with benzenethiol, are products resulting from the *addition* of benzenethiol to the COT substrate. An addition product such as that derived from the following reaction seems plausible.



Support for this speculation is found in the work of Simonson,[4] who isolated this addition product (along with other compounds) from the photolytic reaction of **1** in benzenethiol.
(10) If our speculation regarding the structure of the oils obtained in the reaction of **1** with benzenethiol is correct (vide supra), the corresponding addition product from **2** follows from the parallel reaction.



(11) It is clear from the NMR comparison that the reaction of **1** with thiol produces none of the trapping product from **2**. One may infer then that thiol completely suppresses the rearrangement. The author would like to thank a reviewer for calling attention to this point.
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Kinetic Study of the Relationship of Rearrangement to Racemization in Certain Dibenzo[a,e]cyclooctatetraenes

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The optically active compound (+)-**16**, when heated, gave the racemic form of the expected rearrangement isomer, (±)-**17**. The rate of optical activity loss was approximately 25% greater than the rate of rearrangement. The optically active acid (−)-**23**, when heated, underwent racemization at a rate much greater than the aforementioned rates. These results led to the conclusion that loss of optical activity in (+)-**16** occurs by way of two competing mechanisms. The predominant mode is that of the biradical rearrangement pathway, and the less important mode is that of simple ring inversion. On the other hand, (−)-**23**, presumed to be incapable of racemizing via a reverse rearrangement mechanism, must utilize the more generally recognized ring inversion mode. The extent of this mechanistic dichotomy and its controlling factors are discussed.

Cyclooctatetraene (COT), as the next higher vinylogue of benzene, has been the subject of intensive inquiry since its preparation by Willstatter[1] in 1911. Unlike benzene, its reactions are more typically those of a polyene, reflecting little resonance stabilization or aromatic character. On the other hand, unlike the lower member of the $4n$ cyclopolyene series, cyclobutadiene, COT exhibits none of the characteristic instability or greatly enhanced reactivity which has come to be associated with that series of the $(CH)_n$ hydrocarbons.[2] The absence of so-called antiaromatic properties in COT undoubtedly arises from its nonplanar geometry, in which its "tub" conformation, well-established by the results of electron diffraction measurements,[3] precludes or sharply limits interaction between its π bonds.

Bond angle requirements early suggested that COT might be nonplanar, and before diffraction results became available the question of its geometry was investigated by chemical means, particularly by Cope and co-workers.[4] The substitution of any hydrogen on the COT ring renders the derivative dissymmetric. Cope attempted to resolve such derivatives, as for example, cyclooctatetraenecarboxylic acid, into the optical antipodes. Such attempts were unsuccessful, and this result suggested that the barrier to inversion, if indeed COT was nonplanar, is probably low, less than 20 kcal/mol.

Although the subsequent diffraction experiments provided an unequivocal answer to the question of geometry, there remained the still interesting problem of the energy barrier to inversion in COT. The magnitude of this barrier has been established recently as 14 kcal/mol by means of NMR spectroscopy,[5] but prior to this spectroscopic analysis Mislow and

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